Appendix XIV.4-L

Uranium ~~Bleaching~~Deactivation Process Description

APPENDIX XIV.4-L URANIUM ~~BLEACHING~~DEACTIVATION PROCESS DESCRIPTION

I. Description of Treatment Equipment

The uranium ~~bleaching~~deactivation process is a treatment system used to oxidize uranium chips and mill turnings in a controlled manner. The uranium ~~bleaching~~deactivation process takes place in Building 695 Reactive Materials Cell. The skid-mounted uranium ~~bleaching~~deactivation equipment is operated in the walk-in hood, but it may be stored in the main bay of Building 695 when not in use. The exact design for this treatment process has not yet been finalized. Consequently, all numerical values provided in this process description are approximate and represent expected operations. Additional details regarding the treatment equipment will be provided in the form of as-builts that will be submitted to the California Department of Toxic Substances Control (DTSC) after the equipment is installed.

I.1 Purpose

Lawrence Livermore National Laboratory (LLNL) presently stores uranium chips and mill turnings in liquids (e.g., machining oils and coolants). Finely divided metal will usually be treated for off-site treatment, storage, or disposal. Bulk metal could also be decontaminated for recovery and reuse. In order to dispose or reuse the waste, the oil and coolants must be removed, and the uranium deactivated through an oxidation process.

LLNL uses the uranium ~~bleaching~~deactivation treatment process—i.e., a chemical oxidation/reduction reaction that converts the elemental uranium to a stable compound (e.g., uranyl hydroxide or uranium dioxide) that is amenable for disposal. During the treatment process, uranyl hydroxide is immediately removed from the metal surface exposing new metal for further reaction. In the case of finely divided waste, such as uranium turnings, this process will oxidize all of the metal. In the case of bulk metal, this process will oxidize layers of surface metal and will decontaminate the metal for further disposition.

The uranium ~~bleaching~~deactivation treatment system is designed to control the rate of reaction, dissipate exothermic heat generation, and manage product off-gases safely.

I.2 Theory of Operation

I.2.1 Oxidation Reactions

The first step in the chemical process is to use either sodium hypochlorite (NaClO) or hydrogen peroxide (H_2O_2) to oxidize elemental uranium (U) to uranyl hydroxide ($UO_2(OH)_2$). The oxidization reaction is exothermic with the reaction heat estimated to be about 260 kcal per mole of uranium. The two corresponding reactions are shown below.

I.2.1.1 Alternative for Uranium Oxidation Using Sodium Hypochlorite

When sodium hypochlorite is used to oxidize uranium, the result is uranyl hydroxide with sodium chloride as a by-product:

$$U + 3NaClO + H_2O \text{ ---------> } UO_2(OH)_2 + 3NaCl$$

The above reaction is pH sensitive. If the pH of the sodium hypochlorite solution becomes acidic (e.g., pH < 7), UO_2Cl_2 can form. UO_2Cl_2 is very soluble and unstable in aqueous solutions; and when heated, it releases toxic chlorine fumes through decomposition. The formation of UO_2Cl_2 is curtailed by continuously monitoring the oxidation reaction and maintaining the pH of the sodium hypochlorite solution above 9.

Any unreacted sodium hypochlorite is drained from the reactor and reduced by sodium thiosulfate. This reduction reaction is as follows:

$$4NaClO + Na_2S_2O_3 + H_2O \text{ --------> } H_2SO_4 + Na_2SO_4 + 4NaCl$$

I.2.1.2 Alternative for Uranium Oxidation Using Hydrogen Peroxide

The alternative reaction uses hydrogen peroxide to oxidize the uranium to form uranyl hydroxide:

$$U + 2H_2O_2 \text{ ---------> } UO_2(OH)_2$$

In this reaction, no byproducts or toxic intermediates are anticipated.

I.2.2 Reduction Reaction

After one of the two alternative oxidation reaction is used, sodium thiosulfate or sodium thiosulfate pentahydrate may be added to reduce the uranyl hydroxide to uranium dioxide (UO_2). The reduction reaction is as follows:

$$4UO_2(OH)_2 + Na_2S_2O_3 \text{ --------> } 4UO_2 + H_2SO_4 + Na_2SO_4 + 3H_2O$$

Uranium dioxide is insoluble and stable, making it suitable for disposal. Sulfuric acid (H_2SO_4), sodium sulfate (Na_2SO_4), and water are also formed as by-products.

I.2.3 Safety of the Oxidation Process

Uranium oxidizes in the presence of air and water. The heat generated from the oxidation can produce a fire, causing uranium to be considered pyrophoric. The danger of fire increases with higher temperatures, and uranium ignites on contact with a flame. LLNL has mitigated these hazards by storing the uranium chips in liquids (e.g., machining oils and coolants).

The oxidation rate of uranium under normal conditions is low: approximately 0.005-mil depth of oxidation per hour in water. Although uranium stored in water has a higher oxidation rate than when it is stored in air, the water acts as a heat sink.

The light film of oil present on the surface of the uranium from the machining process decreases the oxidation rate even further. An oxide layer that is relatively impervious forms on the outside of the uranium and slows the oxidation rate even further. This oxide layer mitigates the hazard associated with the uranium chips when they are exposed to air. Their exposure to air is also limited by LLNL's handling procedure that transfers the uranium waste to be processed directly from storage containers (via a draining table to facilitate screening) to the ~~bleaching~~deactivation unit. LLNL uses similar handling procedures to consolidate uranium chips, and there have been no instances of fire or noticeable temperature change due to oxidation.

Organic materials in contact with either sodium hypochlorite and hydrogen peroxide pose a fire risk. Consequently, in addition to draining, uranium waste is rinsed with water to remove organic residues prior to the initial oxidation step. (No surfactants or detergents are present in the water.) Rinsing the uranium waste with water is not expected to generate elevated levels of hydrogen that could pose a fire hazard, because the uranium waste has already been immersed in liquids (e.g., machining coolants) while in long-term storage.

The uranium waste to be treated has a low enough surface-area-to-volume ratio that limited exposure to air and water does not pose a significant hazard. Consequently, additional provisions for dehumidification, maintaining an oxygen-free atmosphere, or conducting the emptying and draining process in a glove box is not required.

The oxidation treatment process occurs within a reaction vessel. To prevent the potential for fires or explosions, an inert nitrogen atmosphere is maintained in the vessel. In addition, the uranium waste is treated in small (approximately 80-lb) batches to further minimize the potential for "run-away" reactions.

I.3 Equipment Operations

The uranium chips must first be removed from the liquids before they can be deactivated through the oxidization process. The treatment requires draining the immersion fluid from the chips into a waste container so that the fluid can be reused or subsequently treated. Containers are processed individually. As shown in **Figure 1**, the container is opened, and its contents are emptied onto a draining table either manually or with the aid of the forklift. (To accommodate the forklift, a roll-up door has been installed on the eastern side of the reactive materials cell.)

Figure 2 shows the process flow for the equipment used to treat the uranium wastes. The major pieces of equipment consist of a chemical reagent mixing/feed tank with a minimum capacity of 150 gal, and a reaction vessel with a capacity of approximately 7.5 cubic feet.

Using hand tools, an operator places approximately 80 lb of the uranium waste into the reaction vessel through the vessel head. (Trays and/or baskets may be fabricated to hold the uranium waste and facilitate its removal from the reactor.) Any remaining uranium waste that is not loaded into the reactor is returned to the waste container along with the drained immersion fluid. Once the uranium waste is loaded into the reactor, the vessel head is secured, and the reactor is purged with nitrogen. Nitrogen is used throughout all the treatment steps to ensure that an inert atmosphere is provided. The nitrogen gas originates from a standard, high-pressure gas cylinder. A pressure regulator equipped with a needle valve controls the flow of gas through the reactor.

Process water is added to the system to remove organic residues from the uranium waste. The reactor's agitator may be started to mix the waste and the water, enhancing the organic removal process. When rinsing is complete, spent rinse water is removed from the reactor to a tank or container for further processing in the Liquid Waste Processing (LWP) area, and the controlled reaction between the elemental uranium in the waste and an oxidant begins.

The reactant solution feed pump transports the oxidant—either sodium hypochlorite (NaClO) solution or hydrogen peroxide (H_2O_2)—from the mixing/feed vessel to the reaction vessel. Reagent in excess of the stoicheometric amount is added to maximize the amount of uranium oxidized. It is estimated that approximately 150 gal of oxidant solution is needed to oxidize 80 lb of uranium waste, and the oxidation reaction will be completed in a minimum of two hours.

The oxidant solution is recirculated to enhance the mixing and oxidation process. To cool the solution within the reaction vessel, cold water is typically used in a heat exchanger on the recirculation loop.

As the reaction proceeds, fresh oxidant solution is transferred from the mixing/feed vessel to the reactor via the reactant feed pump(s) to replenish the oxidant solution. As fresh oxidant enters the reactor, an equal portion of spent oxidant solution must be removed. Either a portion of the spent oxidant solution recirculating through the cooling loop is recycled back to the mixing/feed vessel for reuse, or the spent solution is discharged into a liquid waste container.

The temperature of the reaction vessel is continuously monitored. The flow of oxidant to the reaction vessel would be immediately stopped if abnormal readings were observed. If the temperature approaches 140°F, the recirculation rate is increased. If the temperature reaches 180°F, the oxidant is removed from the reactor.

When the oxidation process is completed, the oxidant solution is drained from the reaction vessel to a container for subsequent treatment in the LWPA. If sodium hypochlorite is used as the oxidant, this solution and any spent solution previously drained during the reaction are treated by adding excess sodium thiosulfate.

The last step in the treatment of the uranium chips is the reduction reaction where excess sodium thiosulfate or sodium thiosulfate pentahydrate may be added to form an insoluble stable material suitable for disposal (uranium dioxide [UO_2]). This step is conducted only if needed to meet the off-site TSDF's waste acceptance criteria. The sodium thiosulfate is directly added to the reactor and/or mixing/feed vessel.

An excess amount of sodium thiosulfate is used to drive the reaction toward the production of uranium oxide. Agitation and recirculation are used to provide mixing. When the reaction is complete, the solution is drained from the reactor to a container for subsequent treatment in the LWP area.

The sulfuric acid formed as a byproduct in the reduction reaction may be neutralized with sodium hydroxide (NaOH).

After draining the reactor, the reaction product and associated residues are removed from the vessel and placed into a container. An operator carries out this transfer by disassembling the vessel head, and directly removing the material from the vessel using hand tools or by tipping the reactor onto the draining table. The reaction product may be subjected to further treatment via the solidification process prior to off-site shipment.

I.3.1 Air Pollution Control Equipment

The uranium ~~bleaching~~deactivation process takes place in the reactive materials cell. The reactive materials cell and its walk-in hood are equipped with a common ventilation and off-gas treatment system to handle gaseous emissions. The emptying and draining processes may take place outside of the hood; however, to prevent exposure to potential airborne contaminants, the air flow is directed away from workers.

The off-gas system consists of an acid gas scrubber, HEPA filter, and carbon adsorption columns (see **Figure XIV.4-2**). Because the uranium waste may contain organic materials, the pollution control devices are designed to comply with the requirements of Title 40 of the Code of Federal Regulations (CFR) 264, Subpart CC.

I.4 Types of Wastes to Be Treated

The waste is uranium turnings and chips. Some residual oil may also be present, but the treatment is chemical oxidation of uranium.

II. Effectiveness of Treatment

II.1 Treatment Performance Information

The ~~bleaching~~deactivation reaction temperature is used as the primary indicator of the treatment performance.

II.2 Process Controls and Safety Features

Hydrogen gas may be generated during the oxidation reaction due to the presence of water in the reaction vessel. Sodium hypochlorite also decomposes when heated and can generate oxygen. Because these properties pose potential fire/explosion hazards, inert nitrogen gas is used during the oxidation reaction to purge the reaction vessel.

The uranium ~~bleaching~~deactivation process is a manual operation. The following process controls, instrumentation, and safety features are utilized:

- Temperature within the reactor and mixing/feed vessel is continuously monitored. The flow of oxidant solution from the mixing/feed tank to the reaction vessel is stopped should abnormal readings be observed.

- To minimize potential pressure and temperature rises, administrative controls are used to limit the mass of uranium placed in the reaction vessel.

• In order to protect the reactor, the off-gas vent line is equipped with a pressure-relief device that is set below the design pressure of the reactor.

• To measure the lower explosive limit (LEL), a combustion gas indicator (CGI) or hydrogen meter may be installed in the reactor. If the measurements exceed 10% of the LEL, chemical additions is suspended, and/or the flow of nitrogen purge gas is increased to dissipate the buildup of gases in the reactor.

• To prevent sparking from static electricity buildup, all appropriate equipment is electrically grounded using a common (shared) grounding line.

II.3 Inspections and Maintenance

The reactor and associated lines are pressure-tested prior to use. A test run is also performed prior to initial use to test the pumps, cooling system, and instrumentation. The test is carried out to ensure that all moving parts of the mechanism function correctly and that the instrumentation and control systems operate as designed.

Operators are properly trained prior to being allowed to operate the uranium ~~bleaching~~deactivation process unsupervised. A pre-operational safety inspection is conducted each day that the treatment process is to be used. At a minimum, the following items are visually inspected:

• General condition of the system (e.g., checking for loose fittings or bolts, frayed wires, worn or broken seals, blocked access, etc.)

• Proper functioning of instruments, alarms, interlocks, and emergency shut-off controls.

III. Equipment Specifications

The uranium ~~bleaching~~deactivation equipment is secured to a skid-mounted platform with forklift pockets to allow the system to be easily transported. Except for the nitrogen gas supply, all hardware and local controls are located on the skid. Electric power, process water, and air supplies are from the Building 695 utility systems. The skid anchoring and other structural supports are seismically designed.

The specifications provided below are believed to be representative of the equipment to be fabricated although deviations may be required to match off-the-shelf items. Most deviations will not be significant.

III.1 Reaction Vessel

The reaction vessel has an internal volume of approximately 7.5 cubic feet to allow adequate capacity to process 80 lb of uranium waste per batch. The reaction vessel is equipped with an agitator, an inert gas supply, and a recirculation loop with heat exchanger and recirculation pump (described below). A CGI or hydrogen meter may be installed in the reactor to measure the LEL. The reaction vessel is constructed of a material deemed satisfactory for uranium compounds, peroxide, bleach, thiosulfate, sulfuric acid, sulfates, and sodium chloride at the expected concentrations and operating conditions. Trays and/or baskets may be fabricated to hold the uranium waste and facilitate its removal from the reactor.

III.2 Feed/Mixing Vessel

The mixing/feed vessel has a minimum capacity of 150 gal and is constructed of a material that is compatible with 12.5 wt% sodium hypochlorite. It has an agitator and drains to a pump for delivery of the oxidizing solution to the reactor. The feed pump has a capacity of approximately 14 gpm. The top of the vessel includes a recycle line from the recirculation loop and lines for raw chemical feed additions. The chemical reagent feed pumps are included on the skid. The portable containers for the chemical reagents are located next to the skid.

III.3 Recirculation Loop and Cooling System

The oxidant solution flows through a recirculating loop with a cooling system to remove reaction heat. It is proposed that a water-cooled heat exchanger be used. The expected design flow of the recirculation loop is around 15 gpm.

IV. Equipment Drawings

Equipment drawings for the uranium ~~bleaching~~deactivation skid will be provided to DTSC as as-builts.

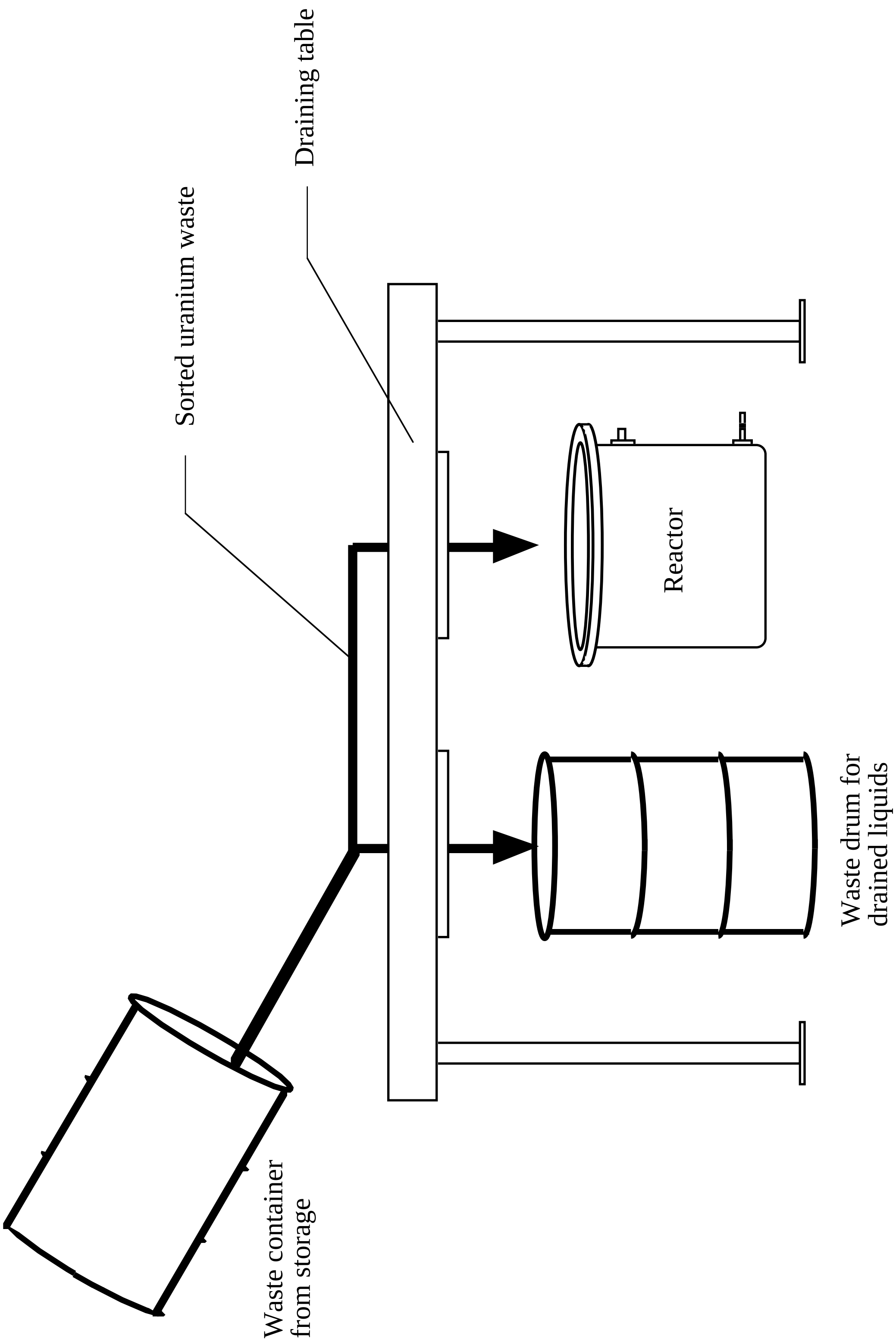

Figure 1. Proposed Process Flow Concept for the Draining Table

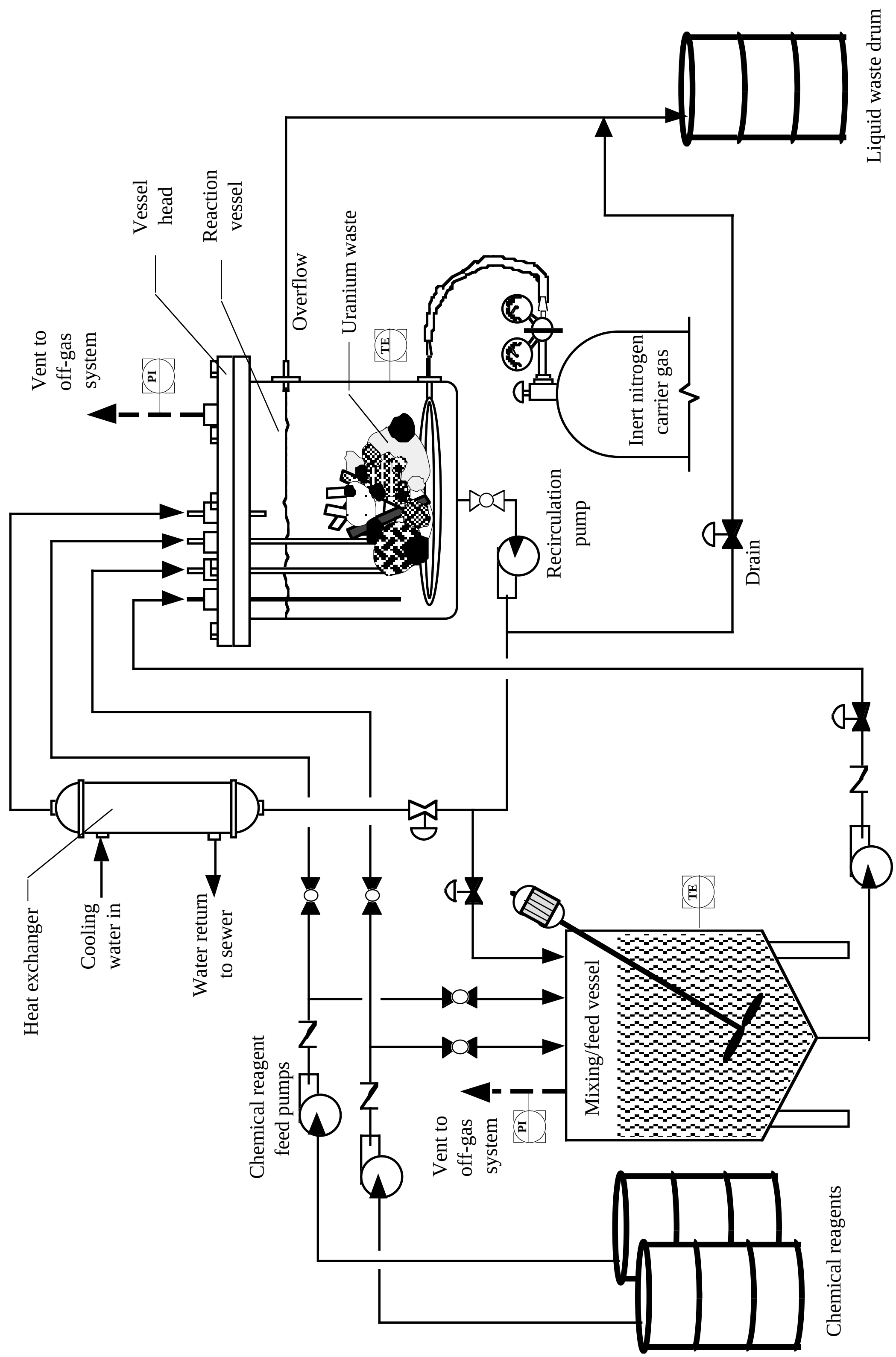

Figure 2. Proposed Process Flow Concept for Uranium ~~Bleaching~~Deactivation